Electronic Supporting Information

Preparation of Dispersible Graphene through Organic Functionalization of Graphene using a Zwitterion Intermediate Cycloaddition Approach

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1. Experimental

Chemicals

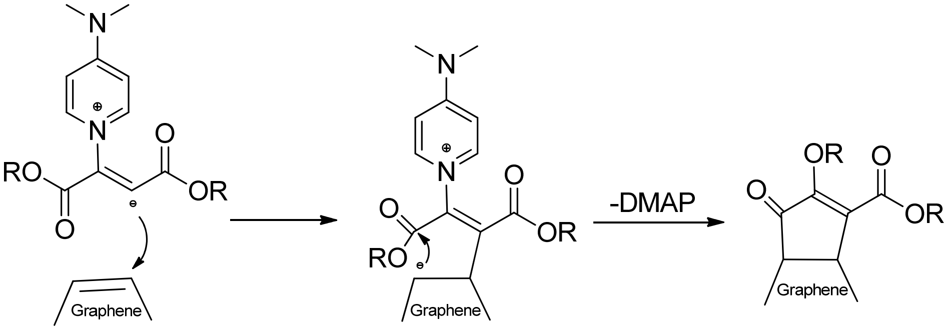
Graphite flakes (Sigma-Aldrich), ortho-dichlorobenzene (ODCB, 98%, AR, Merck), 4-dimethylaminopyridine (DMAP, ≥ 99%, Aldrich), dimethylacetylenedicarboxylate (compound **1**, Sigma-Aldrich, 99%) were used as received without further purification. Dry toluene was used from a solvent purification system (MB SPS-800). Compound **2** was synthesized according to literature procedures.[1]

Instruments

Sonication was conducted with a low-power sonication bath (Bransonic, PC 620). Centrifugation was performed with a Hermle Z323K centrifuge. Filtration was carried out with a Sintered Micro Filter holder through a 0.45 μm nylon membrane. NMR spectra were recorded using a Varian VXR-400 spectrometer (400 MHz). Fourier transform infrared spectroscopy (FTIR) was performed with a Perkin-Elmer Spectrum 400 instrument and a UATR attachment. Raman spectra at 532 nm were obtained using a home built system comprising of a iDus-DU420A CCD detector coupled to a Shamrock163i spectrograph (Andor Technology) and a 25 mW 532 nm DPSS laser (Cobolt Lasers) fibre coupled to an Olympus BX51 microscope (equipped with laserline clean up and edge filters from Semrock) with long working distance objectives. Raman samples were prepared by spin coating a few drops of the graphene and functionalized graphene on fresh gold substrates followed by drying under vacuum. Thermal gravimetric analysis (TGA) was carried out under N_2 with a Mettler Toledo TGA/SDTA851e system. Transmission electron microscopy (TEM) images were taken using a PHILIPS CM12 instrument operating at 120 KV. High resolution transmission electron microscopy (HRTEM) images were taken using a PHILIPS CM120 instrument operating at 120 KV. Conductivity measurement was determined using the standard four-point probe method on a Keithley 2410 Source Meter. The films were prepared by vacuum filtration of the corresponding dispersions of graphene, **1** or **2** functionalized graphene followed by drying *in vacuo* at 60 °C for 48 h.

Preparation of graphene and functionalized graphene

Preparation of graphene in ODCB: Graphite (300 mg) was sonicated for 2 h in ODCB (300 mL), and the obtained suspension was centrifuged at 3000 rpm for 30 min to remove large and thick flakes. The supernatant was decanted to afford graphene in ODCB (the concentration of graphene in ODCB was about 0.01 mg mL^{-1}).[2,3]
Transfer of graphene from ODCB to toluene: Dry toluene was chosen as the solvent for the functionalization reactions. Therefore, a solvent exchange process was carried out to transfer graphene from ODCB to dry toluene.[4] Graphene in ODCB (200 ml) was filtered through a 0.45 µm nylon membrane, then the filter cake was redispersed in toluene (50 ml) with sonication (5 min) and filtered again. This process was repeated twice and the filter cake was dispersed in 30 ml toluene and centrifuged at 4000 rpm for 10 min. The supernatant was decanted and 30 ml dry toluene was added (under Ar atomosphere), sonicated and centrifuged again (this process was repeated twice). Finally, 35 ml dry toluene was added to the solid residue, and the suspension was transferred into a 100 ml three-neck round bottom flask and used for the functionalization reactions.
Functionalization of graphene: Compound **1** (177.6 mg in 5 ml dry toluene) or compound **2** (360 mg in 5 ml dry toluene) and DMAP (153 mg in 5 ml dry toluene) were added dropwise into the above graphene suspension in toluene, and the mixture was reacted at 85 ^{o}C under Ar atmosphere for 3 d. The reaction mixture was filtered through a 0.45 µm nylon membrane and washed subsequently with toluene (3 times), $CHCl_3$ (3 times), water (3 times) and acetone (3 times) using repeated redispersion, sonication, and filtration steps. The final suspension in acetone was centrifuged at 4000 rpm for 20 min and the solid residue was dried under vacuum to afford the desired functionalized graphene products.
Control samples: The covalent linkage between graphene and the organic functional groups was confirmed by control experiments to confirm that the improved dispersibility is not due to physisorption. Compound **1** (177.6 mg in 5 ml dry toluene) or compound **2** (360 mg in 5 ml dry toluene) or DMAP was added dropwise into the graphene suspension in toluene and the mixture was reacted at 85 ^{o}C under Ar atmosphere for 3 d. The handling procedures were as above for the functionalized graphene.



Scheme S1. Proposed mechanism of the zwitterion cycloaddition reaction.[5]

2. Optical images of 1 and 2 functionalized graphene in the solvents

Fig S1. a, b: **1** functionalized graphene dispersion in DMF and $CHCl_3$; c: **2** functionalized graphene dispersion in water.

3. Electron diffraction pattern of graphene and additional TEM images of 2 functionalized graphene in H_2O

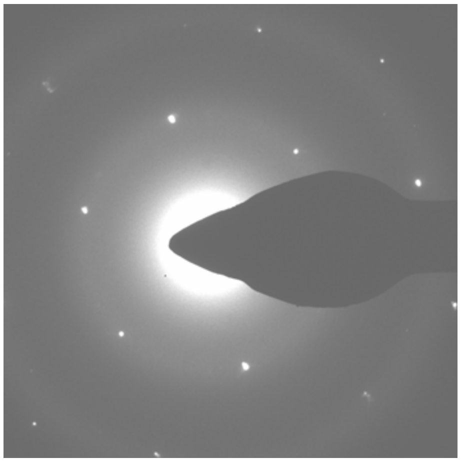


Fig S2. Electron diffraction (ED) pattern of graphene flake shown in Figure 4a. The inner spots intensity is more intense relative to the outer spots intensity, indicating it is a single-layer graphene flake.[2-4]

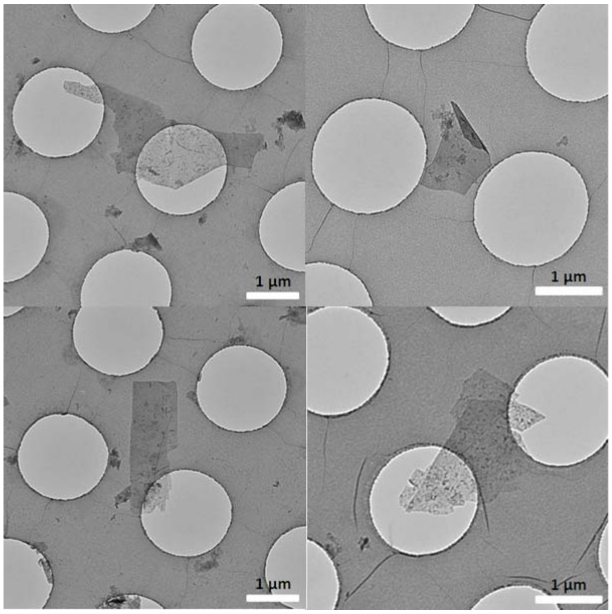


Fig S3. Additional TEM image of **2** functionalized graphene in H_2O.

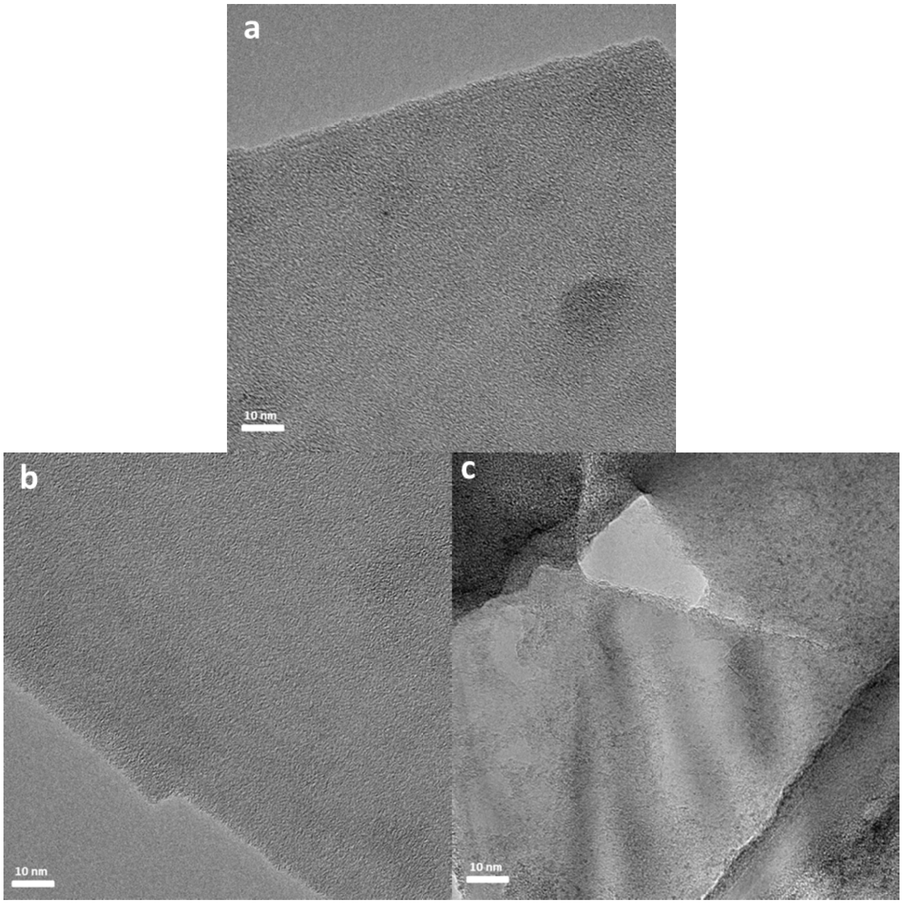


Fig S4. HRTEM images of graphene in ODCB (a), **1** functionalized graphene in DMF (b) and **2** functionalized graphene in H_2O (c).

4. Determination the conductivity of the graphene films

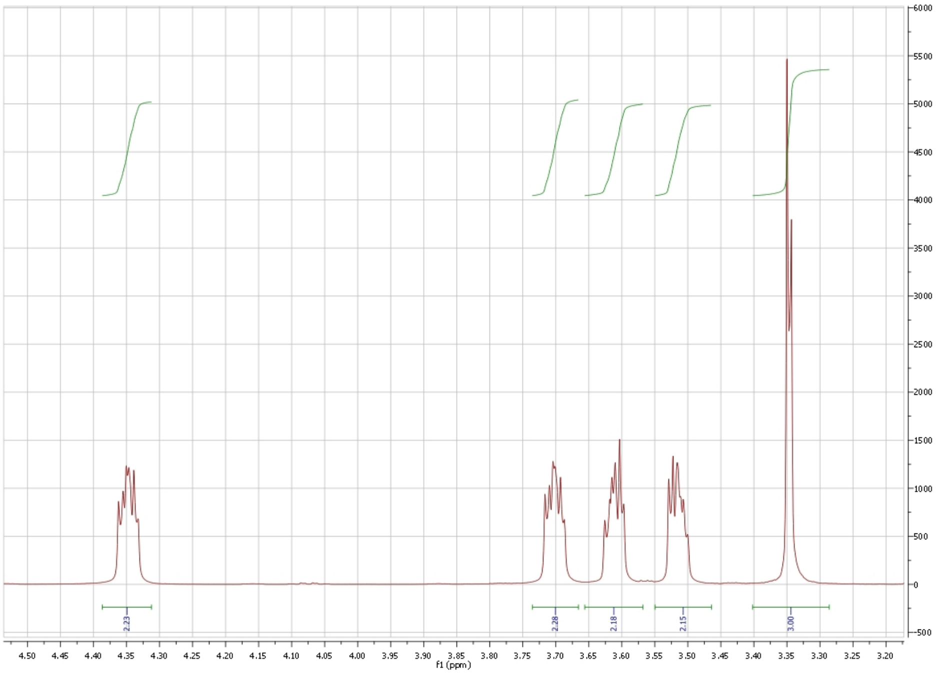
$$\sigma = \frac{1}{R_{\square} h} \qquad h = \frac{m}{\rho_G \pi r^2}$$

σ -conductivity of the films, $R_{\square}$-sheet resistance, h-thickness of the films, m-mass of the films (which was determined by measuring the mass difference of the films before and after filtration), ρ_G-density of graphene (which is 2000 Kg/m^3 according to literature),[6] r-radius of the films.

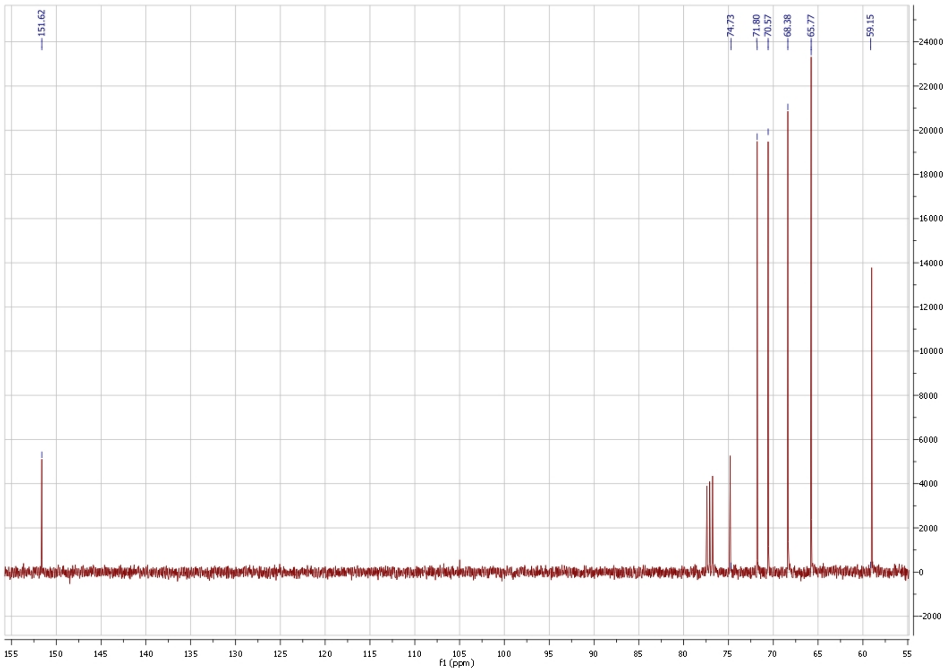
Table S1 Conductivity values of graphene, **1** and **2** functionalized graphene.

Name	$R_{\square}$ (Ω)	σ (S/m)	Average σ (S/m)	Standard deviation of σ (S/m)
graphene	219	3136	3269	±132
	202	3400		
	210	3271		
1 functionalized graphene	77000	7.136	6.88	± 0.36
	85000	6.464		
	78000	7.044		
2 functionalized graphene	1944	684	665	± 20
	2065	644		
	1997	666		

5. NMR spectra of compound 2



^{1}H NMR spectrum of compound **2** ($CDCl_3$, 400 MHz).



^{13}C NMR spectrum of compound **2** ($CDCl_3$, 100 MHz).

References

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